Progress Report

THE PLASTICITY OF MOLYBDENUM SINGLE CRYSTALS

June 1, 1954

I. Polygonization Studies of Bent Molybdenum Single Crystals

II. Research on Twinning in Molybdenum

III. Strain Rate Sensitivity of Molybdenum

Contract Number Nonr 248(05)

NR 039-004

by

K. T. Aust
R. W. Cahn
R. B. Pond

Progress Report

Part I.

Polygonization Studies of Bent Molybdenum Single Crystals

by K. T. Aust

(a) High Temperature Bending

Chen and Maddin[1] previously observed a break-up of Laue spots into small individual areas in a single crystal of molybdenum bent at about 2400° C through an angle of 15°; however, no metallographic observations concerning the presence of subboundaries were reported. The present experiments were conducted to determine whether metallographic techniques would reveal the presence of subboundaries in such a specimen deformed by bending at a high temperature. A single crystal of molybdenum (M-7), which had been bent through an angle of 2° at about 2400° C, was obtained from Dr. N. K. Chen. The specimen was 1/8 inch in diameter x 6 inches long containing a single crystal about 1 inch long in the center section. A Laue back-reflection photogram of the single crystal of M-7 indicated a break-up of Laue spots somewhat similar to that observed by Chen and Maddin[1].

Specimen M-7 was electrolytically polished using an electrolyte of 300 cc methyl alcohol, 60 cc H_2SO_4, 130 cc HCl, and a current density of 4 amp. per sq. cm., and then electroetched with 5% oxalic acid at 4 volts. Metallographic examination revealed the presence of subboundaries in the single crystal section as shown in Fig 1 (a) and (b). Precipitates are visible at the subboundaries (Fig. 1 b) and they appear to occur at certain points spaced almost regularly along the subboundaries. Subboundaries were also observed in the single crystal section adjacent to the polycrystalline end.

Examination at high magnification (X1300) revealed no apparent change of direction of the grain boundary where it meets a subboundary which indicates that the "pull" of a subboundary at the junction is very much smaller than that of a grain boundary.

The dislocation theory of polygonization has been successful in rationalizing the phenomena of straight, parallel subboundaries in the bent crystal experiments of Cahn[2] and of Dunn and Daniels[3]. In the latter experiments, the straight, parallel subboundaries, which were perpendicular to the active slip direction, were observed after simple bending at room temperature followed by high-temperature annealing. The present subboundaries, observed in M-7 after bending at a high temperature, generally form an irregular network which is typical for subboundaries observed under creep conditions. In a few areas in the single crystal of M-7, several subboundaries were observed to be nearly straight and parallel; however, further work is required to determine whether this effect is spurious and if the subboundaries occur perpendicular to the active slip direction.

The present observations simply indicate that subgrains are formed in a molybdenum single crystal when deformed by bending at a high temperature. However, critical experiments are required to determine whether these subgrains are formed directly during high temperature deformation in a single-stage process, or if they are formed as a result of a two-stage process involving deformation by flexural slip, followed by polygonization.

(b) Plastic Bending Followed by Annealing

Previous experiments[4] indicated no evidence of polygonization and recrystallization in single crystals of molybdenum when bent at room

temperature through final angles of about 10° and annealed up to 1000° C for periods of 1 hour. This work was continued by extending the annealing treatments to higher temperatures (1500° C). An annealing furnace was built for this purpose, consisting of glo-bar heating elements and a heating chamber which could be evacuated and filled with argon. A bent single crystal of molybdenum (M-184) remaining from the previous study[4] was annealed in argon atmosphere for 1 hour at 1100° C, 1200° C, 1300° C, 1400° C and 1500° C. X-ray back-reflection patterns were obtained on both the tension and compression sides of M-184 after each anneal. Metallographic examination was also conducted after electrolytic polishing and electro-etching following each anneal. Enlargement of the Laue streaks revealed no evidence of polygonization or sub-grain growth in specimen M-184, i.e. the Laue reflections were not split into separate spots. Also, no microscopic evidence of subboundaries was found after the various anneals up to 1500° C.

Electrical Resistance Measurements

Two bent single crystals of molybdenum, M-83 and M-85,[5] were annealed for 1 hour in argon at 600° C, 800° C, 1000° C, 1200° C, 1400° C and 1500° C. Metallographic, Laue back-reflection studies and electrical resistance measurements were carried out after each anneal. It was believed that electrical resistance might give a sensitive quantitative measurement of the changes occurring during recovery, since electrical resistance recovers at much lower temperatures than hardness and line width in iron and also in nickel, but not in copper[6].

Resistance measurements were made with a Leeds and Northrup Kelvin Double Bridge. A special jig was constructed for holding a bent molybdenum crystal in an identical position for each resistance measurement such that the distance between the potential leads was constant. A current of 5 amperes

was passed through the metal for a period of less than 10 secs. All resistance measurements were made at atmospheric temperature (21° C to 24° C) and were corrected to 21° C. The readings of resistance were accurate to ± 0.000001 ohms. The resistivity values are shown in the following table, and plotted as a function of annealing temperature in Fig. 2. The resistivity values are accurate to ± 0.03 ohm-cm x 10^{-6}.

Electrical Resistivity (ohm-cm. x 10^{-6}) at 21° C

Crystal Condition	Crystal M-83	Crystal M-85
as bent	6.41	6.43
600° C, 1 hr.	6.33	6.43
800° C, 1 hr.	6.33	6.46
1000° C, 1 hr.	6.30	6.43
1200° C, 1 hr.	6.30	6.46
1400° C, 1 hr.	6.27	6.40
1500° C, 1 hr.	6.25	6.45

It is evident that no apparent change in resistivity has occurred in single crystal M-85, although the resistivity of crystal M-83 shows a significant decrease. Crystals M-85 and M-83 were bent at room temperature through angles of 14° and 8° respectively; also, a difference of orientation exists between these two crystals[5]. However, whether the difference in recovery of electrical resistivity between M-85 and M-83 is due to orientation, amount of bending, or some other factor is not known at present. It is interesting to note in this connection that Burgers and his co-workers[7] have found in aluminum a dependency of polygonization on the orientation of the crystal with respect to the direction of deformation. However, Laue back-reflection photograms and microscopic examination showed no evidence of polygonization or recrystallization in the bent

molybdenum crystals, M-83 and M-85, after annealing up to 1500° C.

Future Work

It is apparent that one or more of the conditions necessary for the appearance of subboundaries, such as strong curvature of the crystal and high annealing temperature, have not yet been satisfied. Therefore, further studies will be conducted with greater bending and higher annealing temperatures. X-ray back-reflection and microscopic studies will be continued, together with electrical resistance measurements. It is evident, also, that the above conditions for the appearance of subboundaries are necessary only to reveal subgrains which are few in number and large. A more sensitive technique, such as the focused Laue X-ray method, may reveal the polygonized state after weak curvatures and annealing at lower temperatures. Experiments using more sensitive X-ray techniques will be initiated. Further studies will also be made on the subgrains observed in molybdenum crystals when deformed by bending at high temperatures.

References

(1) N. K. Chen and R. Maddin, "Observations on Cleavage and Polygonization of Molybdenum Single Crystals", Trans. A.I.M.E. (1951), 191, 531.

(2) R. W. Cahn, "Recrystallization of Single Crystals After Plastic Bending", J. Inst. Metals, (1949), 76, 121.

(3) C. G. Dunn and F. W. Daniels, "Formation and Behaviour of Subboundaries in Silicon Iron Crystals", Trans. A.I.M.E. (1951), 191, 147.

(4) K. T. Aust and R. Maddin, "Annealing of Molybdenum Single Crystals After Plastic Bending", Progress Report, The Plasticity of Molybdenum Single Crystals, January, 1954.

(5) K. T. Aust, R. Maddin and N. K. Chen, "Bending of Molybdenum Single Crystals", Trans. A.I.M.E. (1953), J. Metals (Nov.), p. 1477.

(6) C. S. Barrett, "Structure of Metals", 1943, p. 376.

(7) W. G. Burgers, Y. H. Lui and T. J. Tiedema, "The Influence of Crystal Orientation on Polygonization of Aluminum Single Crystals", Proc. Neth. Acad. Science, (1951), 54, 459.

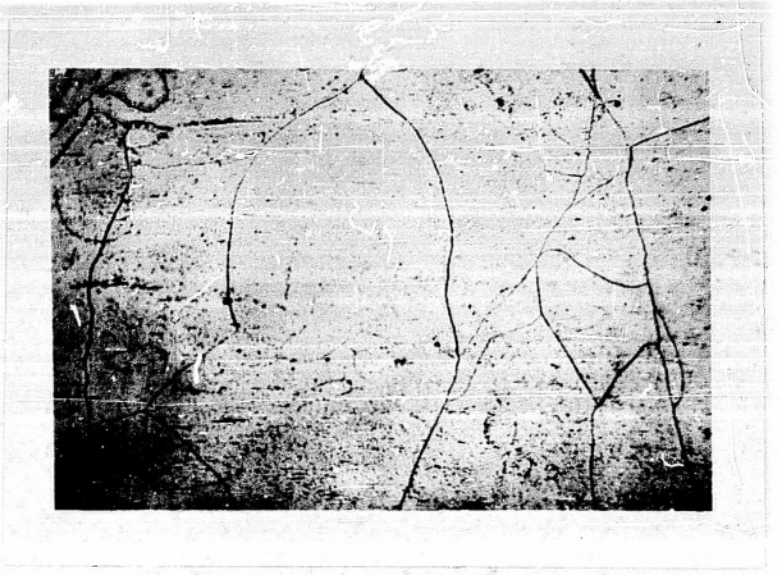


Fig. 1 (a) - Subboundaries in molybdenum single crystal (M-7) deformed by bending at 2400° C. Electrolytically polished and electro-etched 45 secs. in 5% oxalic acid solution at 4 volts. X 300.

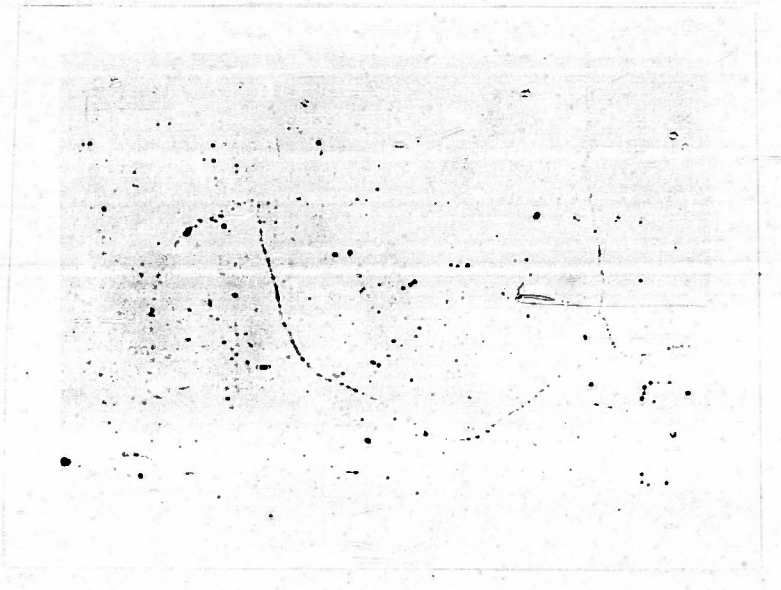


Fig. 1 (b) - Same crystal as in 1 (a), but in a different area. Electrolytically polished and electro-etched 15 secs. in 5% oxalic acid solution at 4 volts. X 500

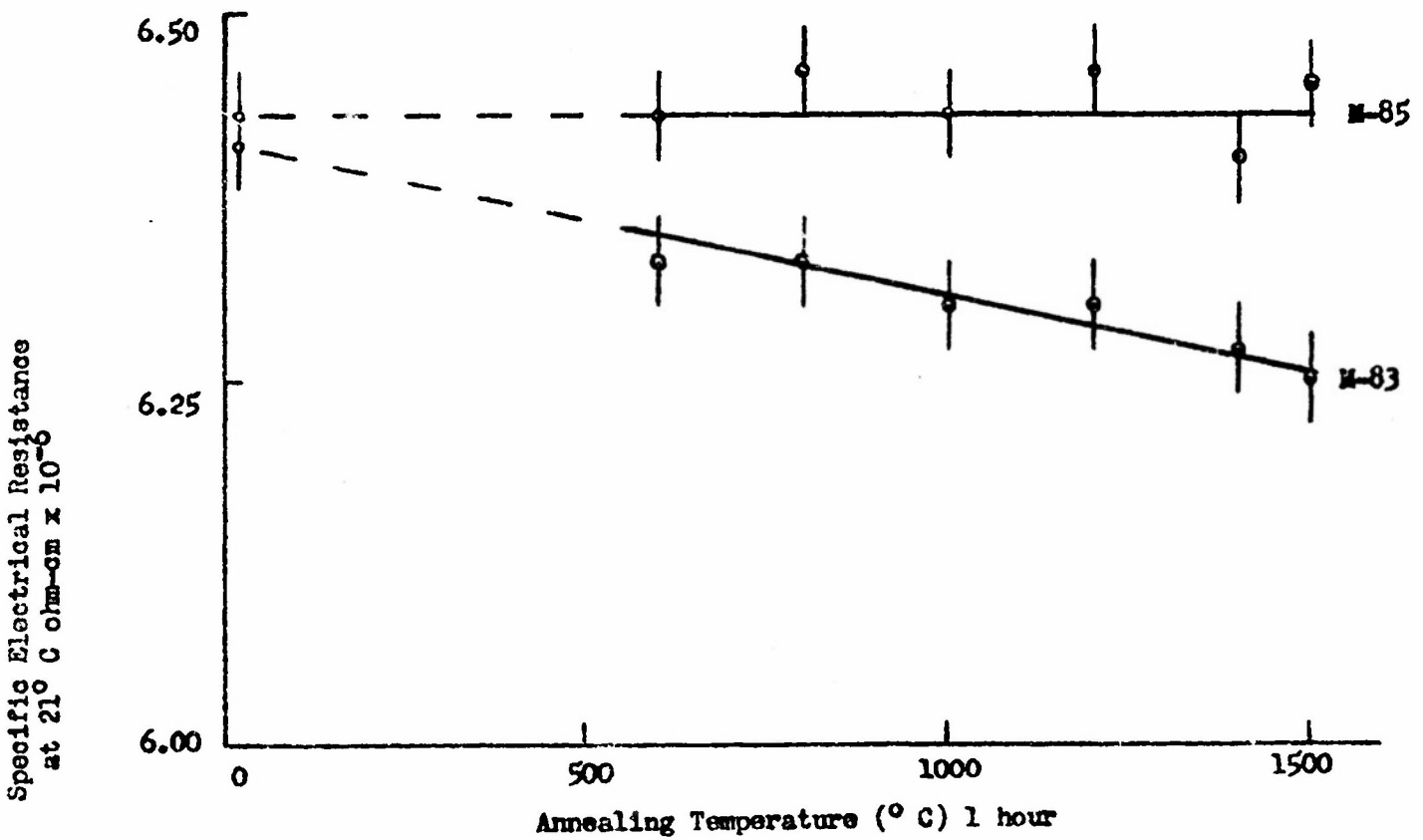


Fig. 2 - Resistivity of Bent Molybdenum Single Crystals after various anneals

Part II.

Research on Twinning in Molybdenum

by R. W. Cahn

A great deal of research has been done on the twinning behaviour in iron, and some evidence has recently been published that twinning is possible in chromium (Carrington, J. Inst. Met., 1953, 82, 170) and molybdenum (Bechtold, Trans. AIME 1953, 197, 1469), metals which have the same structure as iron. Having entered a molybdenum stronghold, I wished to confirm the indications for molybdenum - which consisted of lamellae on an etched section - by proper crystallographic tests.

Some tiny crystals of molybdenum were available, in the form of facetted dodecahedra anything from ½ to 1 mm across the flats. These had been grown by accident during the manufacture of large crystals; metal had evaporated from an overheated part of a molybdenum rod, and had condensed again in the form of a crystal connected to the rod by a slender stem. The faces were all of the (110) family, as would be expected from the fact that these are the most closely packed with lattice points (Bravais' rule).

Since twinning in iron is obtained most easily in single crystals deformed by impact at low temperatures, these conditions were repeated here. Figure 3 shows the apparatus used. The specimen was mounted on the steel anvil by means of cement, so that a facet was parallel to the plane of the mount. Paper was pasted over the aperture of the brass vessel which was then filled with liquid nitrogen until boiling had almost subsided. The striker was then released. The small piece of steel mounted on a spring was intended to prevent heat conduction from the striker to the specimen until after the impact was over.

Numerous samples were tested, and some ten of these contained twins, some copiously so. Some of the others had been struck too gently, some too vigorously so that they disintegrated. The following generalizations can be made:

Small crystals (say 1/3 mm across flats) deformed extensively by slip but did not twin or show any signs of fracture. Reductions in height of more than 50% were observed sometimes, which is truly remarkable when one remembers that molybdenum is generally reckoned to be completely brittle a little below room temperature! One such crystal contained three small twin lamellae and was used for X-ray tests, because the deformation had been light enough to avoid much distortion of shape.

Large crystals twinned if struck vigorously enough. In all such cases bar one, fracture was found to be associated with the twinning. The crystal was generally fractured right through except for a skin cohering surface skin at the two impacted facets. The plane of fracture was macroscopically parallel to (100) and parallel to the direction of compression, which was (110). Fractures also passed from the main crack along some twin lamellae, or went to meet them where the lamellae did not reach to the main crack. Also the main crack sometimes deviated a short way, following accurately the interface between the parent grain and a twin lamella. Twinning and fracture evidently go together, and the last observation shows that some twins at least had formed before the spreading crack had traversed the crystal. However, it is impossible to say whether the stress at the head of the spreading crack was responsible for starting the first twin, which might then propagate faster than the crack. High speed motion pictures seem to offer the only hope of deciding this question.

Slow compression tests were also made at liquid nitrogen temperature through the kind cooperation of Mr. John Hoke. Ductility was still considerable, but there was no trace of twinning - or indeed of fracture.

A few fine slip lines were seen on some samples, but no analysis was made. Some markings visible to the naked eye, apparently parallel to (110) to judge from their appearance on various facets, were seen to be kink bands. It will be interesting to see whether slip lines parallel to (112) can be found, this being the most highly stressed slip plane if compression is normal to (110).

The identity of the twins was firmly established. X-ray photographs taken on a Buerger precession camera, which photographed a layer of the reciprocal lattice normal to the (110) plane which is itself parallel to the direction of impact, showed clearly a number of extra spots which a simple analysis showed could only be due to material twinned according to the two twin planes which had been observed on the specimen surface. The advantage of the precession over the Laue method is that monochromatic radiation is used in the forward direction, and there is no continuous background worth speaking of to obscure the faint extra spots. The exposure was some 60 hours.

The surface tilt at the twin bands was also measured on the microscope, using the graduated fine focussing wheel, and found to be about 32° on the average, which was within some 2° of the calculated tilt, assuming the mechanism was as in iron. The sense of tilt was correct. The twinning planes themselves (to be precise, the planes of the lamellae) were found to be parallel to (112), as in iron, and the two planes universally observed were those out of the 12 planes of this form which were most highly stressed (resolved along twin plane and direction).

Further studies are planned for the late summer.

(a) Steel anvil and crystal
(B) Steel spring and separator

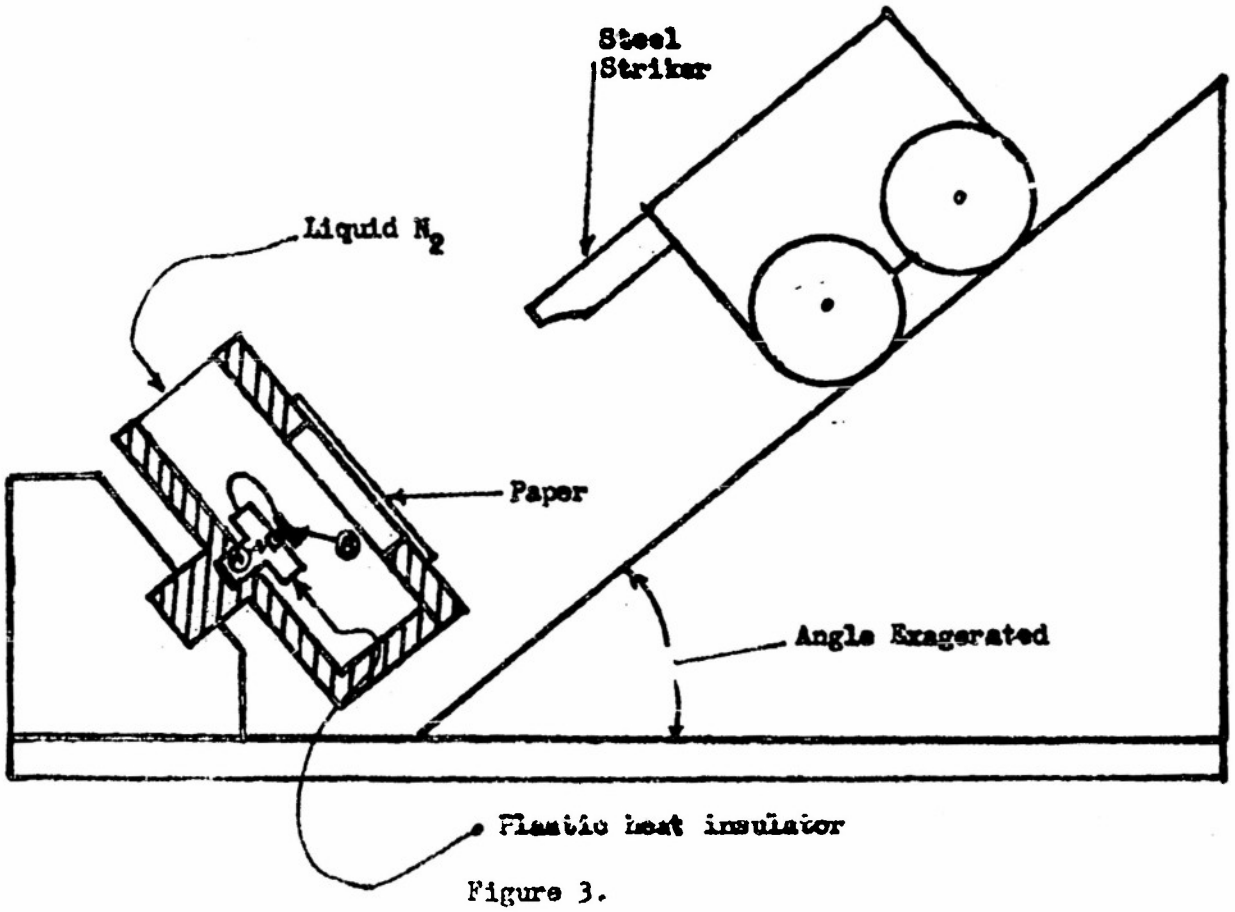


Figure 3.

Part III.

Strain Rate Sensitivity of Molybdenum

by R. B. Pond

The investigation of the strain rate sensitivity of molybdenum as a function of O_2 content and grain size has been continued. The relative grain size of each of seven different groups (of six specimens each) had been varied by annealing at different temperatures prior to innoculation with O_2. However, the entire batch of specimens was inadvertently annealed at a high temperature prior to the O_2 innoculation treatment. The result of this treatment was to minimize the grain size difference in the specimens Despite the small resulting difference in the grain sizes, the test program was continued with the hope that the effect of grain size would not be too subtle to reveal a difference in the effect of the O_2 content on the physical properties when run at varying strain rates.

Each specimen was electrolytically etched in oxalic acid and a grain count taken over the center two inches. String blocks were glued on the center 1½ inches of each specimen to provide for the attachment of a clip-type strain gauge.(1) The specimens were deformed to rupture in a mechanical Olsen testing machine. Good readings were recorded from a Baldwin U type load cell with a Foxboro Dynalog Recorder as strain readings were similarly recorded on a second Foxboro Dynalog Recorder. By arranging for a zero time index on the two machines, it was possible from the two recordings to plot a stress-strain diagram for each specimen. From these diagrams the apparent yield point, ultimate strength and % elongation have been taken and are presented in Table #1. An index of the grain size was developed by counting the grains at the point of rupture and dividing this number into the original

(1) "Dynamic Formation of Slip Bands in Aluminum", N. K. Chen and R. B. Pond, Journal of Metals, October, 1952.

cross-sectional area. This area per grain is presented in Table #1.

Figure 4 is a plot of the % elongation V_S the strain rate for each oxygen innoculation treatment with the grain size index noted for each point. Figure 5 is a similar plot showing ultimate strength V_S the strain rate, and Figure 6 a similar plot showing the apparent yield point. Because of the small difference in grain sizes, three dimensional plots of the above relations have been built in which grain size was the third coordinate and strain rate the second coordinate represented in each case and either % elongation, ultimate strength or yield strength the first coordinate. Unfortunately these plots have not greatly assisted in analysing the data developed.

Macro graphs have been taken of each fractured facet and these closely scrutinized for any differences in the fracture behavior which might be noted. Several pertinent observations should be noted. Some of the fractures developed indicate that almost the entire cross-section of the specimen was a single crystal with one or more very tiny grains evident at the surface of the specimen. In most instances, even with the high O_2 content specimens, fracture would be of the intergranular type for the small grains and of the intragranular type for the large grain or grains. It was recalled that for the slow strain rates, rupture could be anticipated because of an audible clicking or cracking just prior to rupture. It is believed that the intergranular failure occurred first and then served as a notch for the rest of the test. As soon as the intergranular failure occurred, the test being performed was no longer an axial test and erratic results could be expected. On many of the O_2 treated specimens, whole grains would fall from the outside of the specimen at the point of rupture. In every such case the grain was of a wedge shape with the point of the wedge at the interior of the specimen.

Conclusions:

(1) From the plot of % elongation Vs strain rate, it is concluded that there is a progressive detrimental influence of O_2 on the ductility of molybdenum.

(2) Because of the large grain size and the small difference in the grain size from specimen to specimen, no real quantitative analysis can be performed.

(3) The method of approach is sound and a reperformance of the program utilizing closer control on the grain size will produce worthwhile quantitative results.

Table #1

Spec. #	O_2 Treatment Microns	Yield Point p.s.i.	Ultimate Strength p.s.i.	% Elongation	Grain Area Inches	Strain Rate /sec.
264	Vac.	25420	50200	4.07	.00423	.00057
291	Vac.	20750	44700	3.175	.00344	.0036
276	Vac.	16500	64017	4.61	.00226	.0063
265	Vac.	17500	35000	.661	.01973	.010
274	Vac.	15000	25882	.0884	.00531	.025
246	.05	23000	53900	12.370	.00556	.00018
248	.05	25500	63500	15.30	.00690	.00057
247	.05	16300	24850	.0763	.00965	.0017
249	.05	11750	31900	.2530	.00673	.0036
252	.05	15000	21450	.0672	.00575	.0063
250	.05	18500	20850	.0841	.01018	.010
251	.05	12200	23750	.1202	.00593	.025
255	.075	6980	49850	5.67	.00658	.00057
259	.075	15800	22850	.0542	.00972	.0017
268	.075	7750	21950	.1288	.01057	.0036
257	.075	12500	36730	.4635	.02071	.0063
258	.075	14000	18400	.0758	.01140	.010
256	.075	16500	37000	.2302	.01033	.025
271	.1	22500	45300	11.82	.02222	.00018
270	.1	?	24930	.1825	.01983	.00057
269	.1	10610	45600	3.405	.00490	.0017
273	.1	18250	31000	.1010	.01053	.0036
260	.1	10500	38130	.1710	.0128	.0063
261	.1	9500	24410	.1413	.01075	.010
286	.1	?	22450	.0112	.00812	.025
262	.3	19610	53200	10.33	.01274	.00057
263	.3	4500	20330	.0194	.02041	.0017
289	.3	5500	36130	.2221	.02283	.0036
275	.3	3710	39220	.1136	.00714	.0063
272	.3	7500	27900	.0728	.00967	.010
277	.3	15000	49300	.3133	.00697	.025
292	.5	11680	27185	.1225	.01241	.00057
293	.5	8500	37650	.3039	.00654	.0017
267	.5	5250	46800	.6820	.01332	.0036
278	.5	28680	29200	.0616	.01919	.0063
285	.5	5000	25350	.1126	.00917	.010
287	.5	2385	30095	.0648	.00839	.025

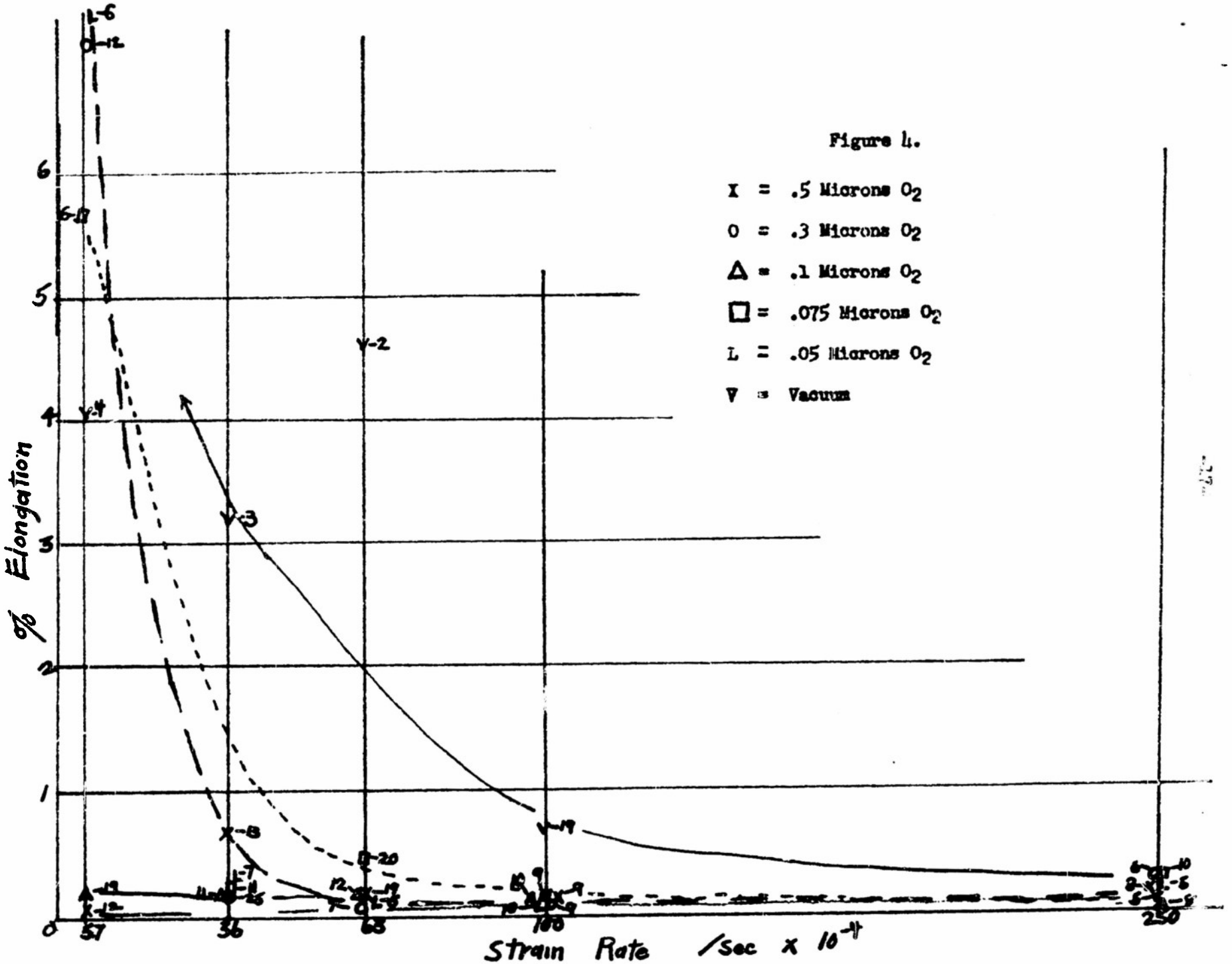

% Elongation
Strain Rate /sec x 10^{-4}
0
1
2
3
4
5
6
57
36
68
100
250
X = .5 Microns O_2
O = .3 Microns O_2
Δ = .1 Microns O_2
□ = .075 Microns O_2
L = .05 Microns O_2
V = Vacuum

Figure 4.

Figure 5.

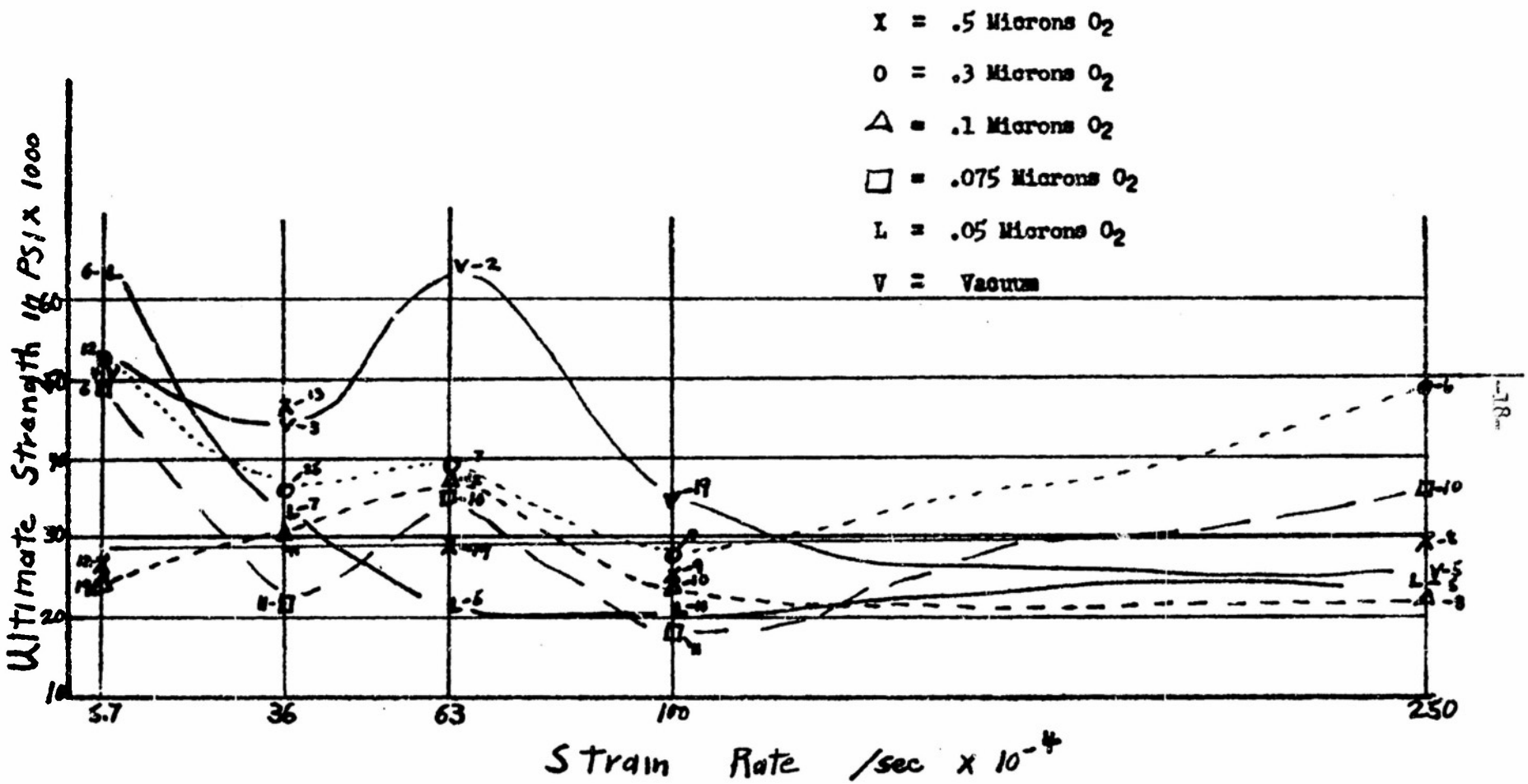
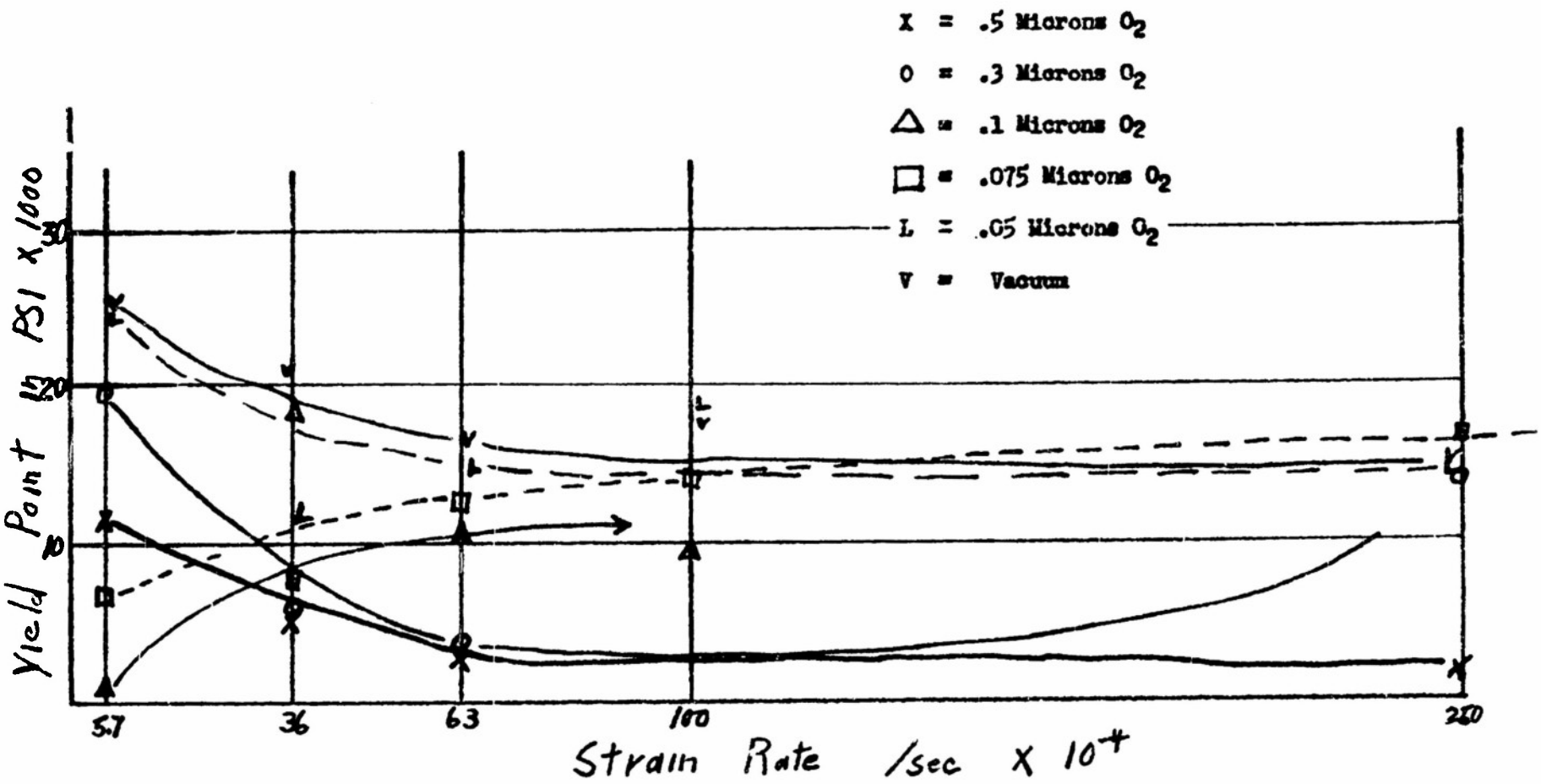

X = .5 Microns O_2
O = .3 Microns O_2
Δ = .1 Microns O_2
□ = .075 Microns O_2
L = .05 Microns O_2
V = Vacuum
Ultimate Strength 1g PSI x 1000
Strain Rate /sec x 10^{-4}
5.7
36
63
100
250

Figure 6.


X = .5 Microns O_2
O = .3 Microns O_2
△ = .1 Microns O_2
□ = .075 Microns O_2
L = .05 Microns O_2
V = Vacuum
Yield Point PSI X 1000
20
10
5.7
36
63
100
200
Strain Rate /sec X 10^{+4}

DISTRIBUTION LIST - Progress Reports - Contract Nonr 260(05), NR 039-004

Air Force	
Wright-Patterson Air Force Base, Dayton, Ohio, Mr. J. B. Johnson	1
Wright Air Development Center, Mr. I. Perlmutter	1
Wright-Patterson Air Force Base, Power Plant Laboratory	1
Army	
Office of Chief of Ordnance (ORDTB), Washington, E. L. Hollady	2
Ordnance Department, Springfield, Mass., Mr. H. P. Langston	1
Watertown Arsenal, Watertown, Mass., P. Kosting	1
Atomic Energy Commission	
Oak Ridge National Laboratory, Metallurgical Div., W. D. Manly	1
Navy	
Bureau of Ordnance, Dept. of the Navy, Re9a (John S. Nachtman)	1
Chief, Bureau of Ordnance, Navy Dept., Re5	1
Bureau of Aeronautics, Navy Dept., N.E.Promisel, Attn: Technical Library, TD-41	1
Naval Base Station, Philadelphia, Attn: Aeronautical Materials Lab.	1
Office of Naval Research, Navy #100, New York	2
Office of Naval Research, Chicago, Attn: Mr. J. A. Bryson	2
Chief of Naval Research, Dept. of the Navy, Attn: Code 423	2
Naval Research Lab., Attn: Code 3500, Met. Div., Code 2020, Technical Library	2
Bureau of Ships, Navy Dept., Attn: Code 343	3
Jet Propulsion Laboratory, California Institute of Technology	1
ONR London, for transmittal to Armament Research Establishment	1
Commander NAMTC, Pt. Mugu, California, Attn: Engineering Dept.	1
Miscellaneous	
Battelle Memorial Institute, Columbus, Ohio, Attn: Mr. Harry Goodwin	1
Bethlehem Steel Company, Bethlehem, Pa., Attn: Dr. John Marsh	1
British Joint Service Mission, Washington, Attn: Navy Staff	3
California Institute of Technology, Attn: Professor Pol Duwez, Metallurgical Dept.	1
Climax MolybdenumCorporation, New York, Attn: Mr. Carl M. Loeb, Jr.	1
Bureau of Standards, Chemistry Division, Washington, Attn: Dr. A. Brenner	1
Climax Molybdenum Corporation of Michigan, Detroit, Attn: Mr. A. J. Herzig	1
Fansteel Metallurgical Company, Illinois, Attn: Dr. F. H. Driggs	1
General Electric Research Laboratory, Schenectady, Attn: Mr. R. M. Parke	1
Lewis Flight Propulsion Laboratory, Cleveland	1
National Advisory Committee for Aeronautics, Washington	1
National Advisory Committee for Aeronautics, Attn: Mr. Eugene B. Jackson	1
Department of Metallurgy, Ohio State University, Attn: Dr. Rudolph Speiser	1
Westinghouse Research Laboratories, East Pittsburgh, Attn: Howard Scott	1
Bureau of Mines, Albany, Oregon, Attn: Dr. S. M. Shelton	1
Mr. H. R. Warfield, I.C.R.	1
Mr. A. P. Ashton, I.C.R.	1